Short communication

Two unsymmetrical lithium organoborates with mixed-ligand of croconato and oxalicdiolato or benzenediolato for lithium battery electrolytes

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HIGHLIGHTS

► Two new lithium salts, (LOCB) and (LBDCB), are synthesized.
► The salts are thermally stable and soluble in organic solvents used in batteries.
► Correlation between the HOMO energy and the electrochemical stability is established.

ARTICLE INFO

ABSTRACT

Two new unsymmetrical lithium salts, lithium (oxalicdiolato croconato)borate (LOCB) and lithium (1,2-benzene-diolato(2-)-o,o' croconato)borate (LBDCB), are synthesized and characterized. The thermal characteristics of them, and their derivative, lithium bis(croconato)borate (LBCB), are examined by thermogravimetric analysis (TG). The thermal decomposition in air begins at 186 °C, 250 °C, and 265 °C for LBDCB, LBCB and LOCB, respectively. The order of the stability toward the oxidation of these organoborates is LBCB > LOCB > LBDCB. The cyclic voltammetry study shows that the LOCB and LBDCB solutions in propylene carbonate (PC) are stable up to 5.1 and 3.7 V versus Li^+/Li. They are soluble in common organic solvents. Ionic dissociation properties of them are examined by conductivity measurements in PC, PC + ethyl methyl carbonate (EMC), PC + dimethyl ether (DME), PC + ethylene carbonate (EC)+ DME, PC + EC + EMC solutions. The conductivity values of the 0.10 mol dm^{-3} LOCB and LBDCB electrolytes in these solutions are lower than those of LBCB electrolytes.

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1. Introduction

Many researchers have attempted to develop improved electrolytes for lithium batteries with high energy density and long cycle life [1–3] as power sources for portable electronic instruments and electric vehicles in order to protect the environment and natural resources. Barthel et al. reported a new class of electrochemically and thermally stable lithium salts [4,5] with a chelate-type boron-containing anion, such as lithium bis[3-fluoro-1,2-benzenediolato(2-)-O,O]borate(FLBBB) [6]. Xu et al. also reported lithium bis(oxalate)borate (LBOB) and lithium [malonato oxalato] borate (LMOB) as advanced electrolytes for Li-ion battery [7,8]. Recently, a novel lithium salt, lithium oxalyldifluoroborate (LODFB) [9], has drawn intensive attention because of its significant merit such as (1) the ability to support metallic lithium cycling reversibly

on the surface of copper anode current collector, (2) the ability to passivate aluminum cathode current collector at high potentials, (3) the ability to participate in formation of the SEI and support Li-ion battery operating stably at high temperatures, and (4) the ability to increase battery safety protection and overcharge tolerance [9–12]. The common feature of these anions is that extensive charge delocalization is present in them because they are composed of strongly electron-withdrawing substituents. Thus, the lithium salts of these anions yield sufficiently high ionic conductivity in solutions, which exhibit wide electrochemical stability windows and good thermal stability.

Based on our previous theoretical studies [13–19], anions with pronounced charge delocalization, $C_2O_4^{2-}$[dianion of oxalic acid], $C_6H_4O_2^{2-}$[dianion of 1, 2-benzenediol], and $C_5O_5^{2-}$ [dianion of croconic acid], are chosen as the unsymmetrical chelators to coordinate with boron to form lithium salts in this study to further our understanding on the relationship between the property and structure of these lithium salts. Two new lithium salts, lithium (oxalicdiolato croconato)borate (LOCB) and lithium (1,2-benzene-

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diolato(2-)-o,o' croconato)borate (LBDCB), as shown in Fig. 1, were synthesized. Their thermal and electrochemical stabilities, conductivities in some solvent mixtures were studied and compared with those in the LBCB electrolytes.

To understand the properties of these new lithium salts at a quantum chemistry level, the density functional theory (DFT) B3LYP method was chosen. We will address the relationship between molecular structures and properties regarding the BDCB⁻, OCB⁻, and BCB⁻ anions and their lithium salts.

## 2. Experimental and computational methods

2.1. Synthesis

LOCB was synthesized according to reaction (1):

$$H_2C_5O_5 + LiOH + C_2H_2O_4 + H_3BO_3 \rightarrow Li\,[B(C_5O_5)(C_2O_4)] + 4H_2O \qquad (1)$$
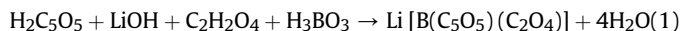
Specifically, 0.02 mol oxalic acid, 0.02 mol croconato acid, 0.02 mol lithium hydroxide, 0.02 mol boric acid, and 22 ml distilled water were transferred into a flask fitted with a reflux condenser. The heterogeneous mixture was heated up to boiling under purified nitrogen, until a homogeneous solution was obtained. The solution was refluxed for 6 h. Thereupon 20 ml toluene was added and the reaction mixture was slowly heated up to 115 °C where a clear brown solution was obtained. After removing 23.3 ml water from the solution within 20 h and cooling down to room temperature, a straw brow precipitate was observed. Then the mixture was stored in a refrigerator at 2 °C for 14 h. After filtration, a solid was obtained. It was purified by multi-time recrystallizations by dissolving into acetonitrile (AN) and drying in vacuo at 80 °C for 48 h followed by 100 °C for 48 h. After drying in vacuo, the product was translated into glove box. The yield for the purified salt was up to 71.2%. The purity of the compound was examined by inductively coupled plasma (ICP, Poasma—Spec) analysis for Li and B contents, which were measured as Li 2.68% and B 4.44%. These data were close to the calculated values Li 2.82% and B 4.40% for LOCB. ESI-MS, m/z for LOCB: 239 (M − Li)⁻.The ¹³C NMR spectra (DMX-500, Bruker) of the prepared solid in (referenced to TMS in dimethyl sulfoxide (DMSO-d6)) gave four signals at chemical shifts of 171.06 (C6/C7), 160.02 (C5), 159.22 (C3/C4), and 157.06 (C1/C2) ppm. The ¹¹B (referenced to BF3·Et2O) NMR spectra gave one signal at chemical shifts of 16.40 ppm.

LBDCB was synthesized according to reaction (2):

$$H_2C_5O_5 + 0.5Li_2CO_3 + C_6H_6O_2 + H_3BO_3 \rightarrow Li[B(C_5O_5)(C_6H_4O_2)] + 3.5H_2O + 0.5CO_2 \qquad (2)$$
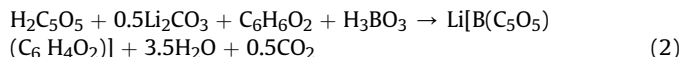
Specifically, 0.1 mol 1, 2-benzenediol, 0.1 mol croconic acid, 0.1 mol boric acid, and 120 ml toluene were transferred into a flask fitted with stirrer and water separator. After heating to 60 °C under purified argon, first of all approximately 0.01 mol of Li₂CO₃ were added using a solids dosing bulb. Within half an hour, no significant formation of gas could be established. Thereupon, 0.45 ml of H₂O was added with a syringe. The reaction now began immediately, with strong formation of gas. Within 5 min, the remaining amount of Li₂CO₃ (in total of 0.05 mol) was added. The gas was thereby formed. The reaction mixture was then heated to boiling point and refluxed for 4 h. After 4 h of refluxing, no more water precipitated. After cooling down to room temperature, a white precipitate was observed. After filtration, a solid was obtained. It was purified by multi-time recrystallizations by dissolving into acetonitrile(AN) and drying in vacuo at 90 °C for 6 h followed by 110 °C for 8 h. After drying in vacuo, the product was translated into glove box. The yield for the purified salt was up to 79%. The purity of the compound was examined by ICP analysis for Li and B contents, which were measured as Li 2.51% and B 4.10%. These data were close to the calculated values Li 2.61% and B 4.07% for LBDCB.ESI-MS, m/z for LBDCB: 259 (M − Li)⁻. The ¹³C NMR spectra of the prepared solid (referenced to TMS in DMSO-d6) gave six signals at chemical shifts of 162.4 (C5), 161.6 (C3/C4), 159.9 (C1/C2), 158.3 (C6/C7), 113.5 (C10/C11), and 103.1 (C8/C9) ppm. The ¹H NMR spectra gave a singlet at chemical shifts of 6.22 ppm. The ¹¹B (referenced to BF3·Et2O) NMR spectra gave one signal at chemical shifts of 12.30 ppm.

The Xray tests of precursors and salts, LOCB and LBDCB, are arranged, as shown in Fig. 2. Comparing the peaks of LOCB, H₂C₂O₂, H₂C₅O₅ and LiCO₃, we can get the result that the prepared compounds are pure LOCB, not the precursors. When we comparing the peaks of LBDCB, C₆H₆O₂, H₂C₅O₅ and LiCO₃. The result that the prepared compounds are pure LBDCB, not the precursors can also been got.
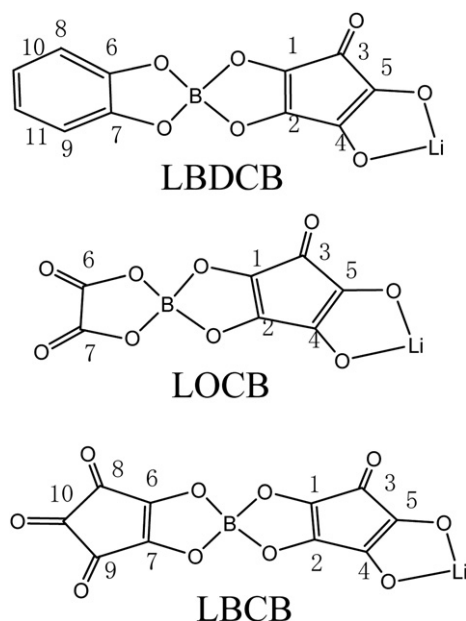

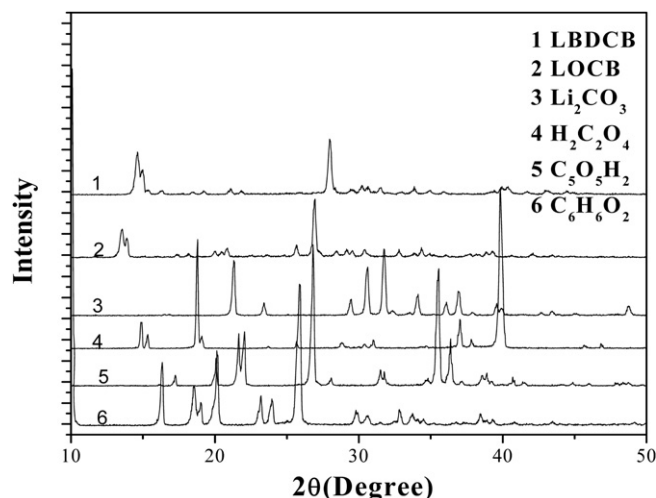
Fig. 1. Structures of LBDCB, LOCB, and LBCB.

Fig. 2. XRD patterns of LBDCB, LOCB, and their precursors.

Meanwhile, LBCB was synthesized with the procedures described previously [14]. The purification procedures for propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), ethyl methyl carbonate (EMC), were the same as given in Barthel et al.'s paper [6].

Excess amounts of solid compound (LBDCB, LOCB and LBCB) are placed into 5 mL vials containing solvent (PC, PC + EMC, PC + DME, PC + EC + DME, PC + EC + EMC). The vials are sealed and placed into a glove box at 25 °C for 6 days, and stirred for a while each 12 h until equilibrium is evident. The upper clear solution is taken for measuring solubility by ICP analysis for Li and B contents.

Thermogravimetric analyses (TGA) of the LBDCB, LOCB, and LBCB were carried out with Perkin−Elmer Pyres-1 DMDA-V1 model, using a sample of about 10 mg. The decomposition voltages (i−E curves) of the electrolytes using a three-electrode system (platinum wire with a surface area of 4.91×10^{-4} cm^2 as working electrode, andLi plate as both counter and reference electrodes) were measured at a scan rate of 9 mV s^{-1}. The preparation of the electrolyte solutions and the cell assembly were carried out in a glove box (Labmaster 130, MBRAUN) at low water(<1 ppm), and oxygen(<1 ppm) contents.

2.2. Computation

The local minima of the complexes have been fully optimized by analytic gradient techniques. The method used was the density functional theory (DFT) with Becke's three parameters (B3) exchange functional along with the Lee-Yang-Parr (LYP) non-local correlation functional (B3LYP). All of the complexes were treated with DFT method at B3LYP/6-31++G(2df,2p) level for full geometry optimization. Nature population analysis (NPA) and natural bond orbital (NBO) [20] analysis were performed at B3LYP/6-311++G(3df,3pd) level using NBO program to obtain quantitative analysis of cation−anion interactions between NBOs of the complexes.

Single-point energy calculations were performed to obtain more accurate binding energies at higher level basis set (B3LYP/6-311++G(3df, 3pd)//B3LYP/6-31++G(2df,2p)), which were defined as $E_{bind} = E_{metalcomplex} - (E_{cation-free} + E_{anion-free})$. The HF method at the same level computation was performed at some cases. All of the HF, DFT and NBO calculations were performed using the Gaussian 03 program package [21].

3. Results and discussion

3.1. Thermal stability

Fig. 3 shows the TG curves of the lithium organoborates in N$_2$. It can be seen that the salt decomposition starts to occur at 186, 250, and 265 °C for LBDCB, LBCB, and LOCB, respectively. Therefore, among the three salts LOCB exhibits the highest thermal stability.

There is now a general agreement to link the thermodynamic stability of a chemical species to the HOMO-LUMO gap increase [22]. These energy levels allow one to calculate a chemical reactivity index, the hardness (η) of these anions. Thus, the structures of BDCB$^-$, OCB$^-$, and BCB$^-$ were optimized by B3LYP/6-31++G(2df,2p), and the energy calculations were further performed by HF/6-311++G(3df,3pd). The results are η(5.0862, OCB$^-$) > η(5.0850, BCB$^-$) > η(4.0547, BDCB$^-$). From these values, OCB$^-$ appears the hardest base. According to the HSAB principle, the hard acid Li$^+$ prefers to coordinate with hardest base OCB$^-$, meaning that the most thermo stable lithium salt in the three salts is Li$^+$OCB$^-$.

Furthermore, it seems that the thermal stability depends on the higher conjugate energies of the chelate-type anion with boron

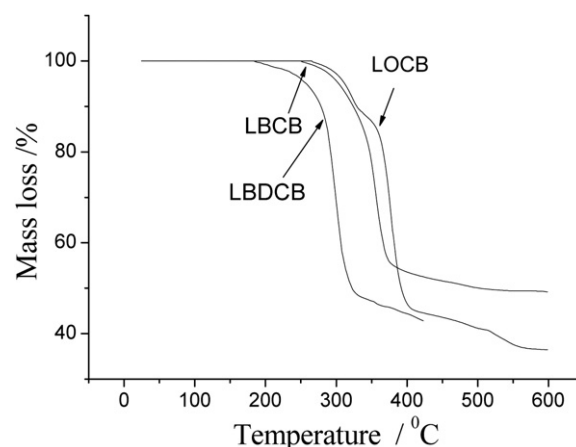**Fig. 3.** TG curves of lithium organoborates at a heating rate of 10 °C min^{-1} in N$_2$ α alumina was used as a reference.

[23]. The higher the conjugation, the smaller the energy difference between HOMO and LOMO. The phenyl group has higher conjugation. So the LBDCB holds the smallest η among the three lithium salts.

3.2. Solubility

Similar to LBCB, LBDCB and LOCB are stable in organic electrolyte solutions but they may be decomposed by hydrolysis in aqueous solutions and converted back to their beginning reactants. They are moderately soluble in PC with a solubility of 0.17 and 0.30 mol dm^{-3} at 25 °C for LBDCB and LOCB, respectively. (Table 1).

As can be seen in Table 1, the solubility of LBCB salt is greater than others in PC solutions. According to our previous theoretical researches [13], we have also chosen to calculate a theoretical set of parameters of TLSER (Theoretical Linear Solvation Energy

Table 1
Solubility, descriptors of anions at B3LYP/6-311++G(3df,3pd) level.

	BCB^{-1}	BDCB^{-1}	OCB^{-1}
S(M, PC, 298.2 K)	0.36	0.30	0.17
Log(S)	−0.44	−0.52	−0.77
μ/Debye	0.00	6.89	0.36
π*/(a.u.)	190.9	187.5	139.2
σ/mS cm^{-1}	2.48	1.00	1.09

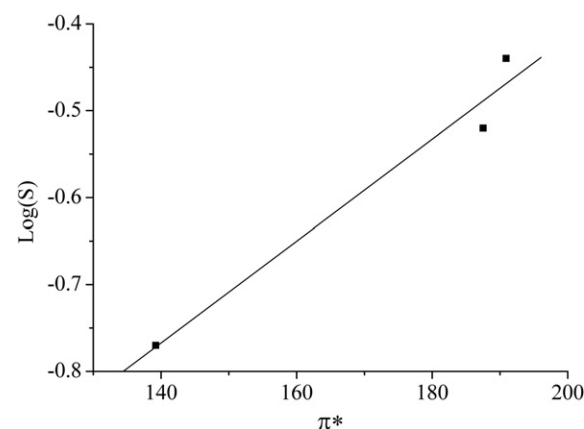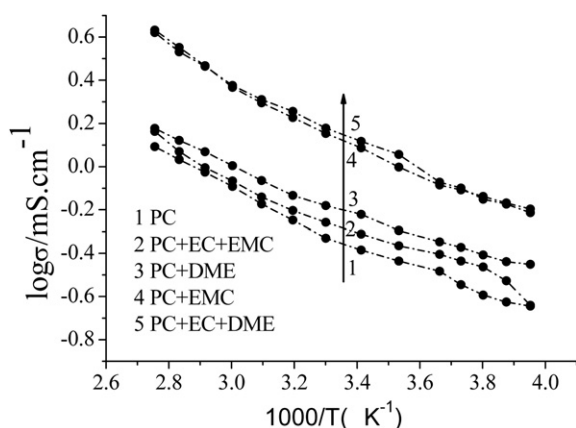**Fig. 4.** The relationship between solubility Log(S) and anion polarizability (π*) of lithium salts.

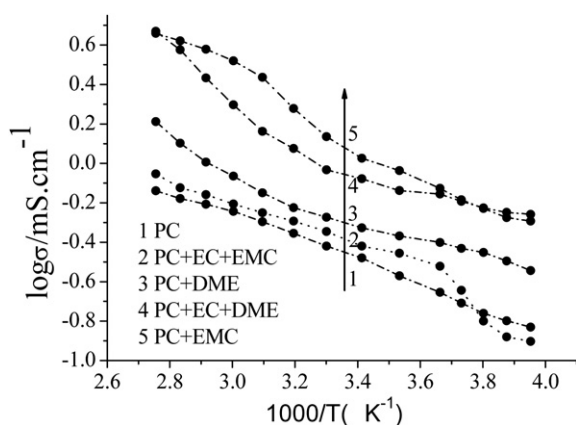**Fig. 5.** Temperature dependence of ionic conductivities of LOCB solutions (0.10 mol dm^{-3}) in different solvents.

Fig. 6. Temperature dependence of ionic conductivities of LBDCB solutions (0.10 mol dm^{-3}) in different solvents.

Relationships), developed by C. J. Cramer et al. [24] and co-workers, and correlated them with the solubility of a lithium salt.

The equation [24] has been applied to the three anions (BCB$^-$, BDCB$^-$, and OCB$^-$). With B3LYP/6-311++G(3df,3pd)//B3LYP/6-31++G(2df,2p)-derived descriptors (Table 1). We obtain a result that the solubility, S, of a lithium salt to be most sensitive to anion polarizability π^* (Fig. 4). The regression is of

$$\log(S) = -1.588 + 0.01\pi^* (R = 0.98, SD = 0.04)$$

3.3. Conductivity

Figs. 5 and 6 show the temperature dependence of ionic conductivity of 0.10 mol dm^{-3} LOCB and LBDCB in PC solvents from −20 to 100 °C. We also include data for solutions in the mixed

Table 3
NBO energetic analysis for LBDCB, LOCB, and LBCB at B3LYP/6-311++G(3df,3pd) level[a](energies in kJ/mol).

	LBDCB	LOCB	LBCB
$n^1o_1 \to n^*_M$	17.47	17.77	16.55
$n^2o_1 \to n^*_M$	10.53	10.45	9.86
$n^1o_2 \to n^*_M$	18.52	16.72	17.59
$n^2o_2 \to n^*_M$	10.95	10.03	10.28
E_{int}	57.47	54.97	54.28

[a] n^1O and n^2O refer to the p lone pairs of the oxygen atoms; n^*_M refers to the antibonding orbital of lone pair of the lithium cation.

solvents of PC + DME, PC + EMC, PC + EC + DME and PC + EC + EMC (mass ratio 1:1 and1:1:1). A 0.10 mol dm^{-3} solution of LOCB in PC shows a conductivity of 0.44 mS cm^{-1} at 25 °C. The solutions of 0.10 mol dm^{-3} LOCB in PC−EMC and in PC−EC−DME have room temperature conductivity of as high as 1.31 and 1.03 mS cm^{-1}, respectively, indicating that the ions in LOCB solutions are highly conductive. As can be seen in Fig. 5, the conductivity of the 0.10 mol dm^{-3} LOCB electrolyte solution in PC−EMC is greater than those in the other solvents.

Table 2 compares the conductivities of 0.10 mol dm^{-3} LOCB solutions in different solvents with those of LBCB and LBDCB. It is clear that LOCB solutions with the same concentration show conductivities higher than those of LBDCB solutions, but lower than those of LBCB. On the other hand, for the saturated solutions of each lithium salt in the solvent of PC, which concentrations are 0.17 mol dm^{-3} for LOCB, 0.30 mol dm^{-3} for LBDCB, and 0.36 mol dm^{-3} for LBCB, respectively, they all have a quite high conductivity, 1.09, 1.00, and 2.48 mS cm^{-1} for LOCB, LBDCB and LBCB, respectively (Table 1).

The disassociation of a lithium salt in the electrolyte solution is one of the key elements affecting Li-ion battery performance. It determines the number of free ions in an electrolyte, and thus the electric conductivity. Makoto Ue analyzed the contribution of the number of ions and the ion mobility to the electric conductivity for a variety of Li-ion nonaqueous electrolytes [25]. He found that the contribution from the number of free ions is generally larger than that from the ion mobility. Thus, the number of ions available plays a major role in determining the electric conductivity of a cell, and hence in the overall battery performance.

As generally recognized, the weaker the coordinating, the easier the separating of an ion-pair is. With the order of $C_6H_4O_2^{2-}$, $C_2O_4^{2-}$, and $C_5O_5^{2-}$, the calculated order of binding energies is $E_{bind}(LBDCB) > E_{bind}(LOCB) > E_{bind}(LBCB)$(Table 3).

Natural bond orbital (NBO) analysis is carried out to further our understanding of orbital interactions and charge delocalization. Of particular interests are the interactions between O (bounded with lithium cation) lone pairs and antibonding orbitals of lithium cation lone pair. The magnitudes of the interactions are shown in Table 3. It is interesting to notice that the calculated order of main orbital interaction energies (E_{int}) is $E_{int}(LBDCB) > E_{int}(LOCB) > E_{int}(LBCB)$, although E_{int} only accounts for part of E_{bind}. In fact, E_{int} may be roughly attributed

Table 2
Total, binding energies of the free anions, their lithium ion pairs at B3LYP/6-311++G(3df,3pd)//B3LYP/6-31++G(2df,2p) level[a].

	Total energy (au)	Binding energies (kJ/mol)	Conductivity(298.2 K, mS/cm)				
			PC	PC + EMC	PC + DME	PC + EC + EMC	PC + EC + DME
LBDCB	−981.06	543.18	0.35	1.20	0.50	0.42	0.88
BDCB^{-1}	−973.56						
LOCB	−976.70	507.13	0.44	1.31	0.63	0.52	1.03
OCB^{-1}	−969.22						
LBCB	−1166.23	486.59	1.32	2.08	1.37	1.37	2.15
BCB^{-1}	−1158.76						

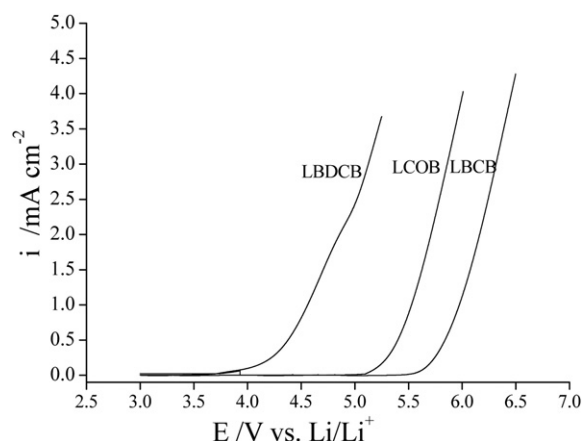[a] $E_{Li+} = -7.28$ (au),Total energy of lithium cation is calculated at the same level.

Fig. 7. i–E curves in PC saturated solutions using a platinum electrodes working at a scan rate of 9 mV s^{-1} at 25 °C.

to the covalency contributions to binding. Thus, the electron transfer from anion (BDCB$^-$, OCB$^-$, BCB$^-$) to Li$^+$ becomes lesser according to NPA and the effective cation charge becomes larger (+0.9551, +0.9569, and +0.9576 e for LBDCB, LOCB and LBCB, respectively). Therefore, BCB$^-$ is the weakest anion of the three salts and Li$^+$BCB$^-$ would be disassociated more than the other two salts at the same concentration of electrolyte solutions. Compared with the calculated data, the experimental conductivity (Table 2) increases with the effective cation charge, and decreases with E_{int} and the extent of electron transfer from anion to cation.

3.4. Electrochemical stability

The electrochemical stabilities of LBDCB, LOCB and LBCB solutions in PC on platinum wire electrode are shown in Fig. 7 and Table 4. The electrochemical oxidation potential can be obtained as ca. 3.7 and 5.1 V vs. Li$^+$/Li for the 0.1 mol dm^{-3} solution of LBDCB

Table 4
Limiting oxidation potentials, HOMO energies using HF methods at 6-311++G(3df,3pd) level.

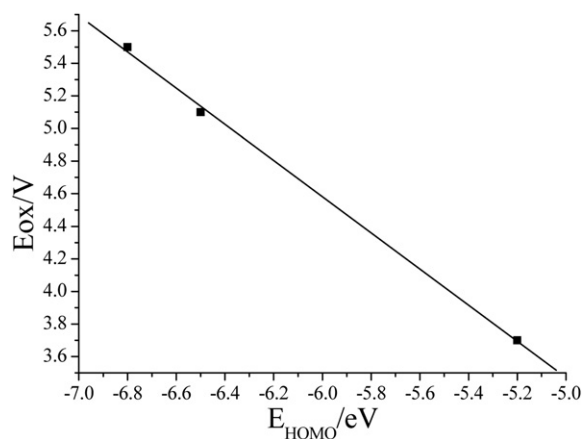| Anion	BDCB$^-$	OCB$^-$	BCB$^-$
E_{HOMO}(eV)	−5.20	−6.50	−6.80
E_{OX}(V vs. Li$^+$/Li)	3.7	5.1	5.5

Fig. 8. Relation between E_{ox} and E_{HOMO} of anions at HF/6-311++G(3df,3pd) level.

and LOCB in PC. The order of the oxidation stability in these organoborates is LBCB > LOCB > LBDCB.

Several studies of anion oxidation potentials were recently updated and extended by Xue et al. [26]. They have found that Eox can be correlated with the E_{HOMO}.

To examine this result, these HOMO energies were calculated using *ab initio* molecular orbital theory. The structure was optimized by B3LYP/6-31++G(2df,2p), and the energy calculations were further performed by B3LYP/6-311++G(3df,3pd). The results are given in Fig. 8, which shows a relatively good linear relationship between the HOMO energies and the limiting oxidation potentials, completely confirming the experimental result: E_{ox}(LBDCB) < E_{ox}(LOCB) < E_{ox}(LBCB). The regression result is

$$E_{ox} = -2.08203 - 1.1106 * E_{Homo}(R = -0.99935, S.D. = 0.048)$$

4. Conclusions

Two new unsymmetrical lithium salts, lithium (oxalicdiolato croconato)borate (LOCB) and lithium (1,2-benzene-diolato(2-)-o,o' croconato)borate (LBDCB), have been synthesized. The salts, LBDCB and LOCB, are thermally stable and soluble in many of the common organic solvents used in batteries. The solutions are highly conductive and stable. The conductivities of LOCB solutions are higher than those of LBDCB solutions. LOCB electrochemical oxidation potential is higher than that of LBDCB in the common organic solvents used in batteries. A strong correlation between the HOMO energy and the electrochemical stability is established. This proves that an extensive charge delocalization, in their anions, caused by strongly electron withdrawing anions (e.g. $C_6H_4O_2^{2-}$, $C_2O_4^{2-}$, and $C_5O_5^{2-}$) would lower the HOMO energy, and improve the electrochemical stability of the electrolyte.

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